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(54) A method for producing zeolite-containing particles.

(57) A method for producing zeolite-containing particles, in which the zeolite has a silica to alumina mole ratio of at least 12, comprises initially compositing seed crystals of the desired zeolite with a matrix material, such that said seed crystals comprise from 0.01 to 2.0 wt. percent of said matrix material, and then preforming the matrix material containing the said seed crystals into particles. The pre-formed particles are then contacted at a temperature of 60°C to 250°C with zeolite producing reactants comprising an alkaline aqueous solution in order to crystallize the required zeolite within said pre-formed particles, the weight ratio of the aqueous solution to said pre-formed particles being from 0.1 to 50, and the pH of the solution being in excess of 7. The resultant particles contain from 3% to 60% of the required zeolite.

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## A METHOD FOR PRODUCING ZEOLITE-CONTAINING PARTICLES

This invention relates to a method for producing zeolite-containing particles.

Crystalline zeolites have been prepared from mixtures of oxides including sodium oxide, alumina, silica and water. More recently clays and coprecipitated aluminosilicate gels, in the dehydrated form, have been used as sources of alumina and silica in zeolite reaction systems.

Seeding is a recognized method of initiating crystallization in zeolite synthesis. Generally in seeding, a small quantity of the desired product is injected into a suitable reaction mixture and, with good mixing, these crystals are circulated to provide nucleation sites for the formation of the net product. U.S. Patent No. 3,671,191 teaches a general seeding technique.

Most commonly, zeolite crystals are incorporated with a binder, i.e. a matrix, to form a catalyst or adsorbant particle. Such matrix is useful not only as a binder, but also to impart greater temperature and impact resistant to the catalyst.

It is recognized in the art that pre-formed catalyst matrix particles can also be transformed under certain conditions into zeolites. The use of matrices to form zeolites is described in many patents including U.S. Patent Nos. 3,746,659; 3,752,772; 3,773,391; 3,694,152; 3,663,456; 3,650,687; 3,647,718; 3,642,662 and 3,545,921. The most common matrix material used in the prior art to form zeolites is a clay, especially kaolin clay.

U.S. Patent 4,091,007 describes an improved method for preparing ZSM-5 by crystallizing a reaction mixture including clay as the major source of alumina, an added source of silica, water and an added source of cations.

The use of pre-formed and high clay content matrix particles places special restrictions on subsequent zeolite crystallization. When clays are used exclusively, the matrix particles tend to be fairly high in aluminum content. Another problem in the use of matrix particles is the tendency for these particles to serve simply as a source of nutrients for crystallization quite exterior to, and physically independent of the original matrix.

It is an object of this invention to furnish a method of fixing siliceous zeolite crystals in a pre-formed matrix. It is further object of the present invention to grow zeolite crystals within a pre-formed matrix, thus forming a matrix-containing zeolite which can be readily used as a catalyst or adsorbant particle. It will be appreciated that whereas conventional techniques for the manufacture of bound zeolite particles comprise two general steps, namely zeolite formation and then incor-

poration of said zeolite in a matrix, the present method allows these two general steps to be combined into a single operation with the attendant benefits of shorter zeolite crystallization time, higher zeolite yields and lower catalyst/absorbent manufacturing costs. An unexpected result of the present method is the unique morphology and crystal size of the resulting zeolite particles.

In accordance with the present invention, there is now provided a method for producing zeolite-containing particles, in which the zeolite has a silica to alumina mole ratio of at least 12, the method comprising the steps of compositing seed crystals of the desired zeolite with a matrix material, such that said seed crystals comprise from 0.01 to 2.0 wt. percent of said matrix material, preforming said matrix material containing said seed crystals into particles and then contacting said pre-formed particles under reaction conditions including a temperature of from 60°C to 250°C with zeolite producing reactants comprising an alkaline aqueous solution to form a reaction mixture in order to crystallize said zeolite within said pre-formed particles, the weight ratio of said aqueous solution to said pre-formed particles being from 0.1 to 50, and the pH of said reaction mixture being in excess of 7, and recovering said particles containing from 3% to 60% of said zeolite.

Thus the present invention provides a method of producing siliceous zeolite crystals, i.e. having a silica to alumina mole ratio of at least 12, within a pre-formed matrix. This is accomplished by depositing seed crystals of the desired zeolite in the pre-formed matrix and then contacting the product with a zeolite forming mixture. Since circulation of the seed crystals cannot occur (since these seed crystals are fixed and imbedded within the matrix), it would seem at first glance that they would not be effective in promoting the crystallization of zeolites. Surprisingly, however, it is found that these imbedded seed crystals are effective in accelerating crystallization of zeolites.

The crystalline zeolites produced by the present method are members of a unique class of zeolitic materials which exhibit unusual properties. Although these zeolites have unusually low alumina contents, i.e. high silica to alumina mole ratios, they are very active even when the silica to alumina mole ratio exceeds 30. The activity is surprising since catalytic activity is generally attributed to framework aluminum atoms and/or cations associated with these aluminum atoms. These zeolites retain their crystallinity for long periods in spite of the presence of steam at high temperature which

induces irreversible collapse of the framework of other zeolites, e.g. of the X and A type. Furthermore, carbonaceous deposits, when formed, may be removed by burning at higher than usual temperatures to restore activity. These zeolites, used as catalysts, generally have low coke-forming activity and therefore are conducive to long times on stream between regenerations by burning carbonaceous deposits with oxygen-containing gas such as air.

With pure zeolite samples, the silica to alumina mole ratio referred to may be determined by conventional analysis. This ratio is meant to represent, as closely as possible, the ratio in the rigid anionic framework of the zeolite crystal and to exclude aluminum in the binder or in cationic or other form within the channels. Although zeolites with a silica to alumina ratio of at least 12 are useful, it is preferred in some applications to use zeolites having higher silica/alumina ratios of at least about 30. In addition, zeolites having very little aluminum, i.e. having silica to alumina mole ratios of 1,600 and higher, are found to be useful and even preferable in some instances.

An important characteristic of the crystal structure of certain zeolites in this unique class of zeolites is that they exhibit selective constrained access to and egress from the intracrystalline free space by virtue of having an effective pore size intermediate between the small pore Linde A and the large pore Linde X, i.e. the pore windows of the structure are of about a size such as would be provided by 10-membered rings of silicon atoms interconnected by oxygen atoms. It is to be understood, of course, that these rings are those formed by the regular disposition of the tetrahedra making up the anionic framework of the crystalline zeolite, the oxygen atoms themselves being bonded to the silicon (or aluminum, etc.) atoms at the centers of the tetrahedra.

Such preferred zeolites have an effective pore size such as to freely sorb normal hexane. In addition, the structure should provide constrained access to larger molecules. It is sometimes possible to judge from a known crystal structure whether such constrained access exists. For example, if the only pore windows in a crystal are formed by 8-membered rings of silicon and aluminum atoms, then access by molecules of larger cross-section than normal hexane is excluded and the zeolite is not of the preferred type. Windows of 10-membered rings are preferred, although in some instances excessive puckering of the rings or pore blockage may render these zeolites ineffective. Al-

though 12-membered rings in theory would not offer sufficient constraint, it is noted that the puckered 12-ring structure of TMA offretite shows some constrained access.

Rather than attempt to judge from crystal structure whether or not a zeolite possesses the necessary constrained access to molecules of larger cross-section than normal paraffins, a simple determination of the "Constraint Index" of the zeolite may be made as described in, for example, U.S. Patent No. 4016218. Preferred zeolites for use in the present method have a Constraint Index of 1 to 12.

Examples of such preferred zeolites are ZSM-5, ZSM-11, ZSM-12, ZSM-23, ZSM-35 and ZSM-38, with ZSM-5 being especially preferred. ZSM-5 is described in greater detail in U.S. Patents No. 3,702,886, Re. No. 29,948, No. 4,139,600 and No. 4,100,262. ZSM-11 is described in greater detail in U.S. Patents No. 3,709,979 and No. 4,108,881. ZSM-12 is described in U.S. Patent No. 3,832,449. ZSM-23 is described in U.S. Patent No. 4,076,842. ZSM-35 is described in U.S. Patent Nos. 4,016,245 and No. 4,107,195. ZSM-38 is more particularly described in U.S. Patent No. 4,046,859.

Useful matrix materials for the pre-formed matrix of the present method include both synthetic and naturally occurring substances, as well as inorganic materials such as clay, silica, and/or metal oxides. The metal oxides may be either naturally occurring or in the form of gelatinous precipitates or gels including mixtures of silica and metal oxides. Non-limiting examples of such porous matrix materials include silica, silica-alumina, silica-thoria, silica-magnesia, silica-zirconia, silica-berylia and silica-titania, as well as ternary compositions, such as silica-alumina-thoria, silica-alumina-zirconia silica-alumina-magnesia and silica-magnesia-zirconia.

Clay materials for use as matrix materials in the present invention include compositions composed primarily of clay minerals identified as hydrated aluminum silicates. Said hydrated aluminum silicate clay mineral may have associated therewith one or more metal or metal oxides selected from the group consisting of Group IA, IIA and VIII of the Periodic Table of the Elements (Sargent-Welch Company, 1968). Non-limiting examples of such hydrated aluminum silicate minerals which comprise the major proportion of clays for use in this invention include kaolinite, halloysite, montmorillonite, illite and attapulgite. Clays containing these minerals are represented by such non-limiting examples as fuller's earth (containing attapulgite with

some montmorillonite), kaolin (constituted of mainly kaolinite) and bentonite (containing appreciable amounts of montmorillonite and usually having some magnesium and iron associated therewith).

Only a small amount of zeolite seeds are needed for the present method, namely 0.01% by to 2.0% of seeds by weight of the matrix. It is preferred to use from about 0.1% to 1.0% of seeds by weight of the matrix. The seed used depends on the zeolite desired to be produced. For example, ZSM-5 seeds produce ZSM-5 zeolite and ZSM-11 seeds produce ZSM-11 zeolite.

It is preferred to form the seeded matrix particles by intimately admixing seed crystals with an inorganic oxide matrix while the latter is in a hydrous state (slurry-type material) such as in the form of a hydrosol, hydrogel, wet gelatinous precipitate, or a mixture thereof. If a hydrosol is formed, it can be permitted to set in mass to form a hydrogel which can thereafter be shaped, dried or spray-dried by conventional techniques. Alternatively, extrusion or pelletizing can be employed to form discrete particles. Once the particle is formed, its dimensions and geometry will be essentially fixed and will not be subject to substantial change during crystallization of the zeolite.

The seeded matrix particles are then contacted with a zeolite forming mixture under the proper reaction conditions to crystallize the desired zeolite within the matrix. In particular, the seeded matrix particles are contacted with an alkaline aqueous-forming solution such that the weight ratio of said aqueous solution to said particles is between 0.1 and 50, preferably between 1.0 and 10. Hydroxide concentration in the initial forming solution will in general, be between 0.01 and 3.0 molar, preferably between 0.1 and 2.0 molar so as to ensure a final pH of solid-solution mixture in excess of 7.0. Preferably, the seeded matrix particles are contacted with the zeolite forming mixture without undergoing an initial calcination step.

Conventional zeolite forming mixtures are employed and comprise sources of an alkali metal oxide, e.g. a sodium oxide, an oxide of silicon (silica), an oxide of aluminum (alumina), water, and, if desired, a source of an organic nitrogen containing cation, such as an amine or diamine; e.g., butylamine, pentanediamine, hexanediamine; a tetraalkylammonium compound, e.g. a tetramethylammonium compound, a tetraethylammonium compound, a tetrabutylammonium compound, or a tetrapropylammonium compound; an

alkylenediamine, e.g. polymethylenediamine; pyrrolidine or a tetraureacobalt (II) complex. In preparation of "extremely highly siliceous" zeolites such as those disclosed in U.S. Patent Re. No. 5 29,948, no source of an oxide of aluminum is employed in the reaction mixture.

The matrix material may also serve as a source of reactants. Thus the matrix may supply all or some of the required silica, alumina, or alkali metal. 10 Additionally the matrix material may contain a zeolite with a silica to alumina mole ratio of less than 12, e.g. a synthetic faujasite type zeolite.

Generally, organic compounds will be present in the initial forming solution in a concentration of 15 between 0.01 and 2.0 molar, preferably between 0.05 and 1.0 molar.

Crystallization is performed either at atmospheric pressure or under elevated pressure in an autoclave or static bomb reactor at pressures in the 20 range of between 100 to 6080 kPa (1 and 60 atmospheres.) Crystallization is generally carried out at a temperature of 60°C to 250°C, but at lower temperatures in this range, e.g. below about 100°C, crystallization time is longer. Typical reaction conditions comprise maintaining the reaction mixture and the seeded matrix at a temperature of 25 80°C to 200°C for 1 hour to 60 days, more preferably at a temperature of 95°C to 160°C for 3 hours to 14 days. Thereafter, the matrix particles containing 30 the crystallized zeolite are separated from the liquid and recovered.

Separation is conveniently effected by cooling the entire mixture to room temperature and then filtering and water washing the solid product. The 35 product so obtained is dried, e.g. at 110°C, for from 1 hour to 8 hours. If desired, milder conditions may be employed, e.g. room temperature under vacuum. The final product is a matrix containing 3% to 60%, preferably 5% to 40% of the required zeolite, with the remainder being the matrix. The 40 final product exhibits unexpected morphology and crystal size.

The following examples will serve to illustrate the invention.

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#### EXAMPLE 1

Two clay-containing catalyst matrices were 50 spray-dried in side-by-side experiments, one containing 1% ZSM-5 crystals, the other containing none. They analyzed as follows:

	<u>With crystals</u>	<u>Without</u>
$\text{SiO}_2/\text{Al}_2\text{O}_3$	5.31	5.70
Surface area ( $\text{m}^2/\text{g}$ ),	204	220

No ZSM-5 was detected by X-ray diffraction in either material. The same clay-containing catalyst matrices utilized in Example 1 were employed in the following Examples 2 to 8. The matrix containing the crystals is referred to as "spray-dried, seeded material" and the matrix without crystals is referred to as "unseeded material".

#### EXAMPLE 2

Twenty grams of spray-dried, seeded material was combined with a solution of 0.20 g NaOH, 1.33 g TPABr and 2.58 g NaBr in 20 g water. The mixture was placed in a steam chest at 95°C. After one week, X-ray diffraction showed the solid to contain 35% ZSM-5. When the same treatment was given to the unseeded material, the solid contained only 15% ZSM-5. Thus the seeded material gave a greater zeolite yield than the unseeded material.

To show that the 35% ZSM-5 sample was not just a physical mixture of crystals with matrix particles, the sample was separated on a 200 mesh screen. The portion passing through 200 mesh analyzed 35% ZSM-5; that retained, 38%.

#### EXAMPLE 3

Twenty grams of seeded material was treated as in Example 2 except that 40 g water was used. After 1 week, the solid contained 30% ZSM-5 whereas the unseeded material had only 10%.

#### EXAMPLE 4

Twenty grams of spray-dried, seeded material was combined with a solution of 2.04 g of 25% TPA hydroxide in 19 g water. The mixture was placed in a steam chest at 95°C. After one week, X-ray diffraction showed the solid to contain 30% ZSM-5. When the same treatment was used on unseeded material, the solid contained only 20% ZSM-5.

#### EXAMPLE 5

Eighty grams of spray-dried, seeded material was combined with a solution of 0.8 g NaOH, 10.3 g NaBr and 5.3 g TPABr in 80 g water. The mixture was placed in a 300 cc stainless steel autoclave and heated 4 hours at 160°C with slow stirring.

5 After cooling, filtering and drying, the product solid contained 16% ZSM-5. When the same treatment was employed with unseeded material, the solid contained only 2% ZSM-5.

#### EXAMPLE 6

10 Example 5 was repeated, but with 0.4 g NaOH, 5.3 g TPABr and no NaBr. After 6 hours at 160°C, the seeded material contained 15% ZSM-5; the unseeded sample contained only 2% ZSM-5.

#### EXAMPLE 7

15 Example 5 was repeated, but with 120 g solid, 1.2 g NaOH, 7.95 g TPABr and 60 g H<sub>2</sub>O. After 6 hours at 160°C, the seeded material contained 15% ZSM-5; the unseeded sample contained only 3% ZSM-5.

#### EXAMPLE 8

20 This Example will serve to illustrate the necessity of alkalinity. The experiment of Example 5 was repeated, but with no NaOH. After 6 hours at 160°C, no crystallinity was found in either the seeded or unseeded matrix.

#### EXAMPLE 9

25 This example shows that the procedures of this invention would not destroy a synthetic faujasite type zeolite if it were present in the precursor composite. 40 grams of NaY were combined with 80 g water and 16.2 g 25% TPA OH. After 6 hours in an autoclave at 160°C, the solid was filtered and dried. X-ray analysis showed it to be 100% NaY.

#### Claims

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1. A method for producing zeolite-containing particles, in which the zeolite has a silica to alumina mole ratio of at least 12, the method comprising the steps of compositing seed crystals of the desired zeolite with a matrix material, such that said seed crystals comprise from 0.01 to 2.0 wt. percent of said matrix material, preforming said matrix material containing said seed crystals into particles and then contacting said pre-formed particles under reaction conditions including a temperature of from 60°C to 250°C with zeolite producing reac-

tants comprising an alkaline aqueous solution to form a reaction mixture in order to crystallize said zeolite within said pre-formed particles, the weight ratio of said aqueous solution to said pre-formed particles being from 0.1 to 50, and the pH of said reaction mixture being in excess of 7, and recovering said particles containing from 3% to 60% of said zeolite.

2. The method of claim 1 wherein the amount of seed crystals comprise is between 0.1 and 1.0 wt. percent of the matrix.

3. The method of claim 1 or claim 2 wherein said zeolite is selected from the group ZSM-5, ZSM-11, ZSM-12, ZSM-23, ZSM-35 and ZSM-38.

4. The method of any preceding claim wherein said reactants comprise sources of an alkali metal oxide, an oxide of silicon, water, and organic nitrogen-containing cations.

5. The method of claim 4 wherein said reactants further comprise a source of an oxide of aluminum.

6. The method of claim 4 or claim 5 wherein said

matrix serves as a source of an oxide of silicon, of an alkali metal oxide and/or of an oxide of aluminum.

5 7. The method of claim 1 wherein the pre-formed matrix is prepared from a clay.

10 8. The method of any preceding claim wherein said reaction conditions include a pressure of between 100 and 6080 kPa (1 and 60 atmospheres) and a contact of time of between 1 hour and 60 days.

15 9. The method of any preceding claim wherein said pre-formed particles are contacted with said zeolite producing agents without an intervening heat treatment step on the particles.

20 10. A process for converting feedstock comprising hydrocarbon compounds to product comprising hydrocarbon compounds of lower molecular weight than the feedstock hydrocarbon compounds which comprises contacting said feedstock at conversion conditions with a catalyst comprising an active form of zeolite-containing particles produced by a 25 method of any preceding claim.

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## EUROPEAN SEARCH REPORT

Application number

EP 86303222.3

DOCUMENTS CONSIDERED TO BE RELEVANT		Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int. Cl.4)
Category	Citation of document with indication, where appropriate, of relevant passages		
A	<p><u>DE - A1 - 3 028 785</u> (ENGELHARD MINERALS &amp; CHEMICALS CORP.)</p> <p>* Claims 1,6,9; page 13, lines 3-19; page 14, lines 7-34 *</p> <p>--</p>	1,7,10	C 01 B 33/28 B 01 J 29/28 C 10 G 11/05 C 10 G 49/08
A	<p><u>DE - A1 - 3 347 123</u> (W.R.GRACE &amp; CO.)</p> <p>* Claim. 1; page 40, lines 24-35; page 41, lines 1-18 *</p> <p>--</p>	1	
A	<p><u>DE - A1 - 2 909 929</u> (BASF AG)</p> <p>* page 2, lines 1-9 *</p> <p>--</p>	1,4	
A	<p><u>US - A - 4 468 475</u> (MOBIL OIL CORP.)</p> <p>* Claims *</p> <p>--</p>	1,5	TECHNICAL FIELDS SEARCHED (Int. Cl.4)
A	<p><u>EP - A1 - 0 134 333</u> (MOBIL OIL CORP.)</p> <p>* Claims *</p> <p>-----</p>	1,5	B 01 J C 01 B
The present search report has been drawn up for all claims			
Place of search <b>VIENNA</b>	Date of completion of the search <b>13-08-1986</b>	Examiner <b>PILLERSTORFF</b>	
<b>CATEGORY OF CITED DOCUMENTS</b>		T : theory or principle underlying the invention E : earlier patent document, but published on, or after the filing date D : document cited in the application L : document cited for other reasons A : member of the same patent family, corresponding document	
X : particularly relevant if taken alone	Y : particularly relevant if combined with another document of the same category		
A : technological background	O : n-n-written disclosure		
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